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(54) **Fluorocarbon-based coating compositions and articles derived therefrom.**

(57) This invention relates to release liners, and more particularly, to release liners suitable for use with highly aggressive pressure-sensitive adhesives. Certain pressure-sensitive adhesives, particularly those derived from silicone resins, are so aggressive that tapes employing them exhibit undesirably high peel forces upon removal from known low-adhesion coatings, especially after prolonged storage or when used in a high-temperature environment. The adhesive of such tapes may carry away, and consequently, be contaminated by appreciable amounts of the low-adhesion material. If this occurs, the tapes will exhibit poor readhesion when applied to "end-use" receptor surfaces. This invention provides curable, crosslinkable compositions and coatings prepared therefrom that can be used to form low-surface energy liners that can be used with aggressive pressure-sensitive adhesives, such as adhesives formed from silicone resins. The release characteristics of these coatings do not diminish upon aging and do not adversely affect the readhesion properties of adhesives that have come in contact with the coatings. The invention further provides substrates bearing a layer of the composition of the invention. These coated substrates are particularly suitable for release liners, especially differential release liners and low-adhesion backsizes for pressure-sensitive adhesive tapes and sheet materials, especially for pressure-sensitive adhesives derived from silicone resins. Because the coatings of this invention can have more than 50% by weight inert oils without significantly reducing the readhesion of adhesives removed from them, they provide an economic advantage over those coatings prepared by using only the more expensive reactive group-containing polyfluoropolyethers.

EP 0 433 070 A2

**FLUOROCARBON-BASED COATING COMPOSITIONS AND ARTICLES DERIVED THEREFROM**Background Of The InventionField Of The Invention

This invention relates to release liners, and more particularly, to release liners suitable for use with highly aggressive pressure-sensitive adhesives.

Discussion of the Art

Pressure-sensitive adhesive tape, which is typically wound into rolls, has a low-adhesion backsize coating applied to the major surface of the backing not bearing adhesive to permit the tape to be unwound without delamination and transfer of adhesive to the surface of the backing not bearing adhesive. The force required to separate the adhesive layer from the low-adhesion backsize coating, i.e., peel force, ranges from 6 to 35 Newtons per decimeter (N/dm) per unit width. If the tape is not wound into a roll, its adhesive layer is customarily protected by a disposable web that bears a low-adhesion coating to which normally tacky and pressure-sensitive adhesives adhere very weakly, e.g., a peel force ranging from about 0.2 to about 6 N/dm, preferably 0.2 to 2 N/dm. Release coatings having peel forces in this preferred range of 0.2 to 2 N/dm are hereinafter referred to as "premium release" coatings.

Release coatings must both adhere strongly to the backing and be sufficiently cured or rendered incompatible with the adhesive so that it does not transfer to the adhesive layer and adversely affect adhesive power of the adhesive. Low adhesion backsize coatings having such properties are disclosed in U.S. Patent Nos. 3,318,852; 3,536,749; 4,057,596; and 4,216,252.

Certain pressure-sensitive adhesives, particularly those derived from silicone resins, are so aggressive that tapes employing them exhibit undesirably high peel forces upon removal from known low-adhesion coatings, especially after prolonged storage or when used in a high-temperature environment. The adhesive of such tapes may carry away, and consequently, be contaminated by appreciable amounts of the low-adhesion material. If this occurs, the tapes will exhibit poor readhesion when applied to "end-use" receptor surfaces.

Known low-adhesion coatings, e.g., poly(urethanes), poly(tetrafluoroethylenes), and poly(dimethylsiloxanes), do not provide release peel forces in the range 0.2 to 2 N/dm when used with poly(dimethylsiloxane) adhesives.

The utility of polymeric fluorocarbons as release coatings has been disclosed in U.S. Patent Nos. 4,472,480; 4,567,073; and 4,614,667. Uncrosslinked fluorinated waxes and oils are frequently used as lubricants and mold release agents in applications where low adhesion coatings are designed to fail cohesively within the bulk phase. Conversely, crosslinked fluorinated waxes and oils are preferred when it is desired to avoid cohesive failure of release liners. Examples of crosslinking reactions that have been used to prepare low energy release liners are photochemical crosslinking, described in U.S. Patent Nos. 4,472,480; 4,567,073; and 4,614,667; thermal crosslinking of silicone resins, described in U.S. Patent No. 4,472,480; and chemical crosslinking of silicone resins (hydrosilation), described in U.S. Patent No. 4,565,741. U.S. Patent No. 4,321,404 describes abherent coatings made by using electron beam radiation to polymerize a mixture of film-forming and polyfluorinated oligomers in a single step. The mixture is formulated so that the fluorinated materials tend to segregate at the coating surface, i.e., the air interface, so that the abherent coating can be crosslinked with a single pass through the electron beam curtain. These coatings have excellent readhesion; however, they were formulated for use with acrylic adhesives and typically have high release values when used with these adhesives. These release values would be higher still if these abherent coatings were used with the highly aggressive silicone pressure-sensitive adhesives.

In order to further reduce the possibility of cohesive failure, a crosslinked primer coating to securely anchor the release coating to its backing has been used. U.S. Patent Nos. 4,567,073 and 4,614,667 disclose the advantage of first photopolymerizing a thin layer of a film-forming polymer that is strongly bonded to the surface of a substrate. This primer layer is also capable of subsequently reacting with functional groups attached to a polyfluoropolyether, which is applied as a second thin layer over the photopolymerized layer, thereby chemically bonding the release coating to the inner primer layer. These release liners exhibit release of about 0.6 N/dm, and excellent readhesion for certain classes of silicone-based pressure-sensitive adhesives.

Summary Of The Invention

The present invention provides curable, crosslinkable compositions and coatings prepared therefrom that can be used to form low-surface energy liners that can be used with aggressive pressure-sensitive adhesives, such as adhesives formed from silicone resins. The release characteristics of these coatings do not diminish upon aging and do not adversely affect the readhesion properties of adhesives that have come in contact with the coatings.

Briefly, the compositions of the present invention comprise a crosslinkable polyfluoropolyether and an inert polyfluoropolyether oil. The compositions can be dissolved in mixtures of fluorinated solvents in order to provide solutions having a viscosity suitable for coating by methods well known in the art.

The composition preferably contains from about 15 to about 90% by weight crosslinkable polyfluoropolyether, more preferably from about 50 to about 85% by weight, and from about 10 to about 85% by weight inert polyfluoropolyether oil. It is preferred that the polyfluoropolyether oil have a viscosity of 20 to 500 centipoise at 25 °C, preferably 90 to 200 centipoise at 25 °C.

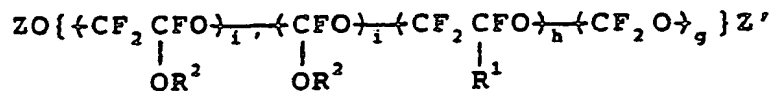
The invention further provides substrates bearing a layer of the composition of the invention. These coated substrates are particularly suitable for release liners, especially differential release liners and low-adhesion backsizees for pressure sensitive adhesive tapes and sheet materials, especially for pressure-sensitive adhesives derived from silicone resins.

Likewise, the release coatings of this invention are specifically formulated and cured to resist cohesive failure within the bulk phase but to fail uniformly along an extremely thin, weak boundary layer at the release coating-adhesive interface.

It has been found that silicone adhesives on the fluorochemical release liners of the present invention will not suffer dramatic reductions of the readhesion value, as will acrylic adhesives on silicone-based release liners if uncured material is present. Surprisingly, pressure-sensitive adhesives in contact with the release liners of the present invention can have very high readhesion values--in excess of 90% of those of control adhesives which have not been in contact with any release coating or liner. Such high readhesion values are indicative of little, if any, transfer of fluorocarbon materials of low surface energy to the pressure-sensitive adhesive. Because the coatings of this invention can have more than 50% by weight inert oils without significantly reducing the readhesion of adhesives removed from them, they provide an economic advantage over those coatings prepared by using only the more expensive reactive group-containing polyfluoropolyethers.

#### Detailed Description Of The Invention

The reactive group-containing, crosslinkable polyfluoropolyethers suitable for use in this invention are represented by the general formula:



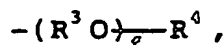
wherein

Z represents a terminal group that either contains a functional moiety that can enter into an addition or condensation reaction to form a polymer or an inert moiety incapable of entering into a reaction to form a polymer;

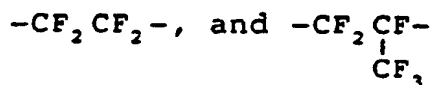
Z' represents a terminal group that contains a functional moiety that can enter into an addition or condensation reaction to form a polymer;

each R<sup>1</sup> independently represents a fluorine or a perfluoroalkyl group that can be linear, branched, or cyclic;

each OR<sup>2</sup> independently represents a perfluoroalkoxy group wherein R<sup>2</sup> represents a perfluoroalkyl group or a perfluoroalkyl group substituted with one or more ether oxygen atoms, independently selected from the units having the structure



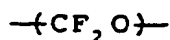
in which each R<sup>3</sup> is independently selected from -CF<sub>2</sub>,



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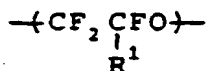
and  $\text{R}^4$  represents a perfluoroalkyl group selected from linear, branched, and cyclic groups,  
 f is zero or a number having a value of 1 to 6,  
 g is a number representing the average number of

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units randomly distributed within the chain and has a value of zero or greater,  
 h is a number representing the average number of

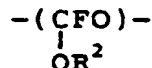
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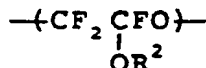
units randomly distributed along the chain and has value of 1 or greater;  
 i and i' can be the same or different and each is a number representing the number of

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and

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units, respectively, distributed within the chain, the sum of i and i' having a value of 0 or greater and the ratio i/i' being 0 to 5;

the ratio of g/h being less than 10;

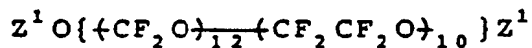
the ratio of (i + i')/(g + h) being 0.0 to 1.5; and

the number average molecular weight of the polyfluoropolyether being from about 650 to 20,000.

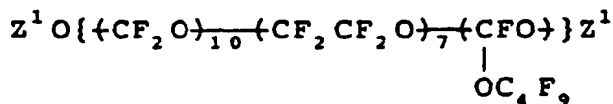
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Especially useful in the practice of this invention are polyfluoropolyether polymers having non-perfluorinated, crosslinkable end groups such as acrylate, isocyanato, or bis(amidopropyltriethoxysilane). Examples of structures of such polymers are as follows:

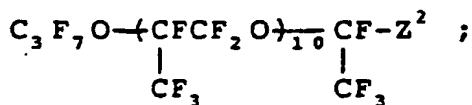
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where

$Z^1$  represents  $-CF_2 \overset{\overset{||}{O}}{C} NH(CH_2)_3 Si(OCH_2CH_3)_3$

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and

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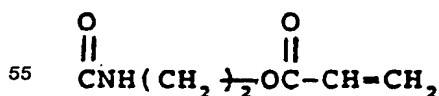
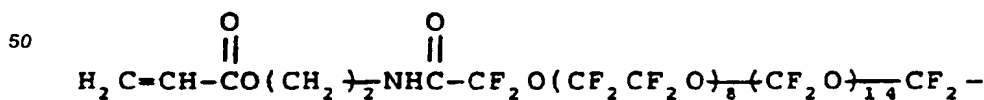
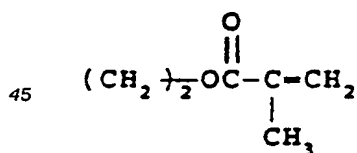
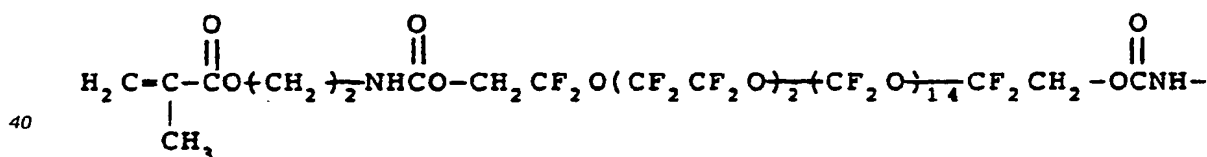
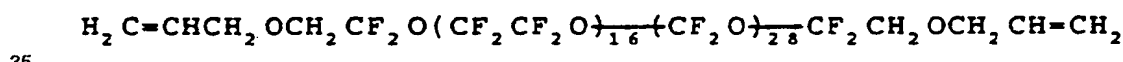
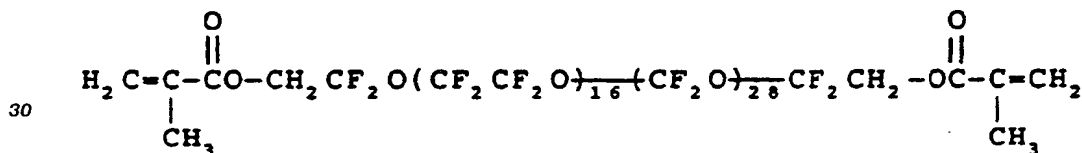
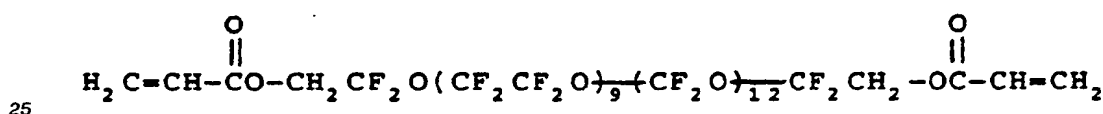
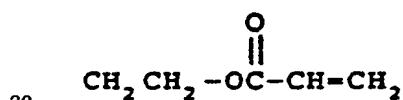
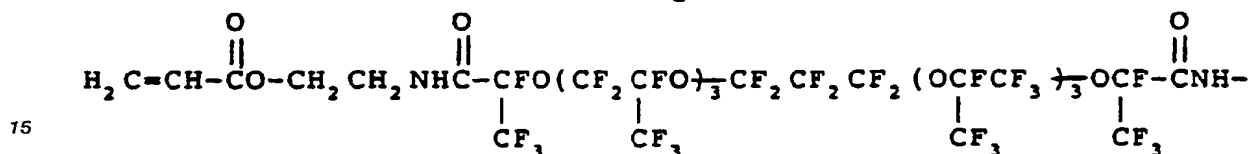
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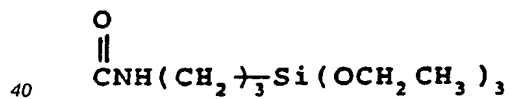
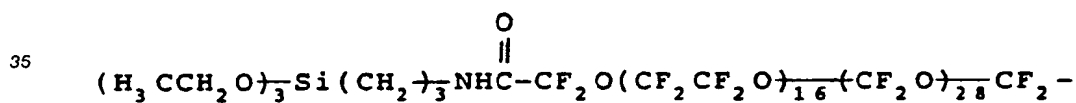
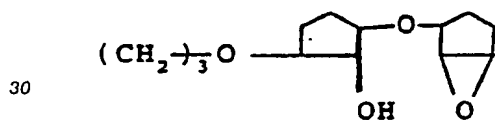
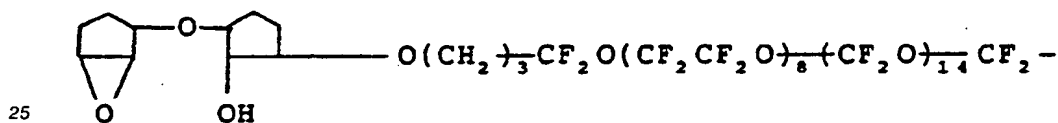
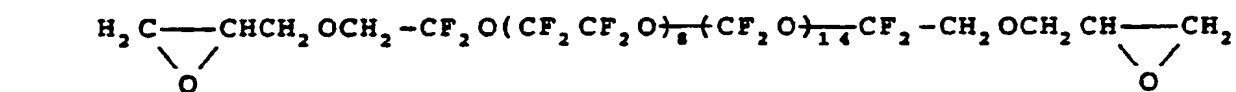
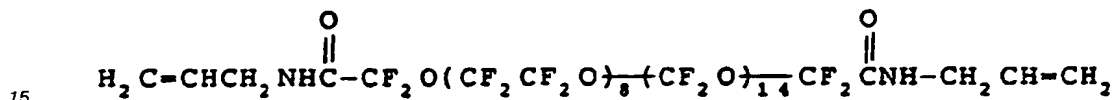
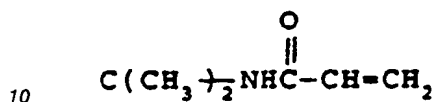
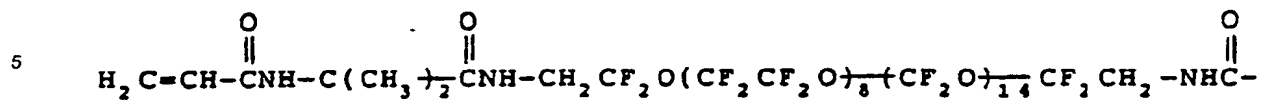
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$Z^2$  represents  $-\text{CNH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$

or

$Z^2$  represents  $-\text{CH}_2\text{OCCH}=\text{CH}_2$

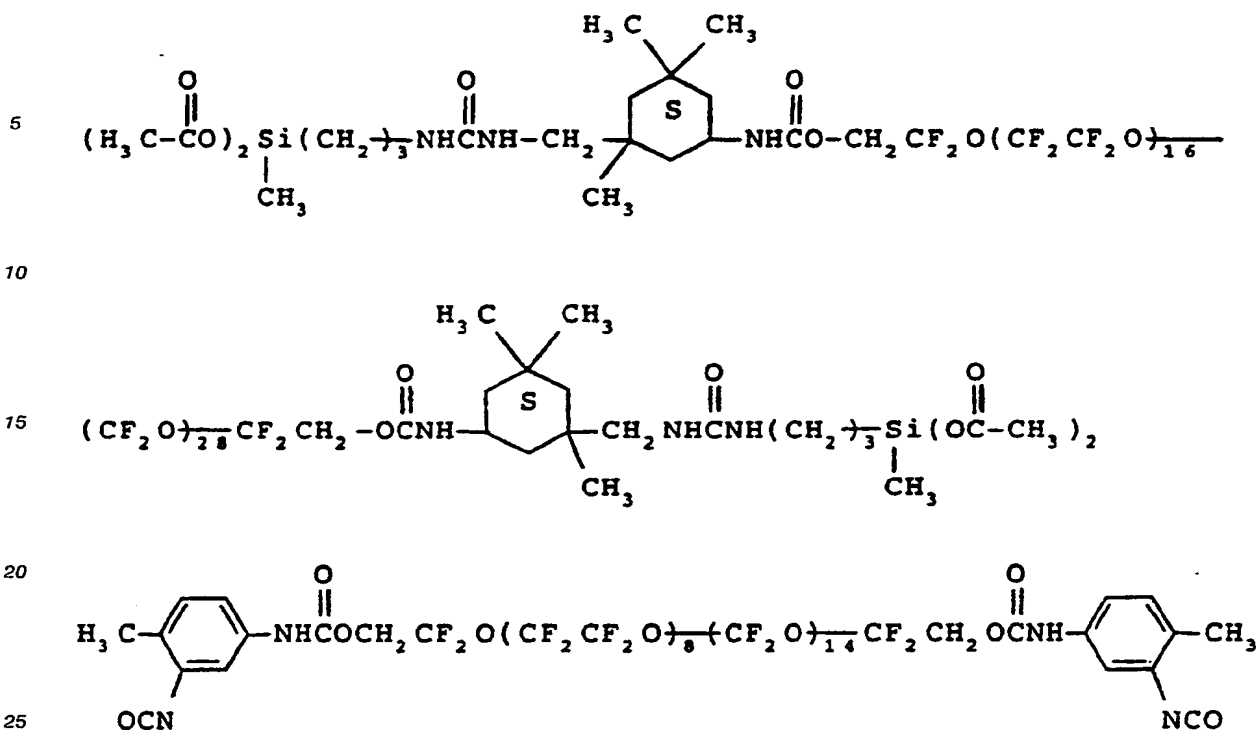




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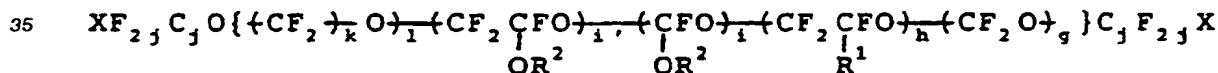
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Many other combinations of crosslinkable end groups and polyfluoropolyether polymer backbones are useful in this invention.

The general formula for inert polyfluoropolyether oils are represented by the general formula:



wherein

each x independently represents hydrogen or halogen, provided that when x represents hydrogen, then j is 1 or 2, and when X represents halogen, then j is an integer from 1 to 5;

R<sup>1</sup>, OR<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, f, g, h, i, i' are as defined previously;

k represents 3 or 4; and

l represents 1 or a number greater than 1.

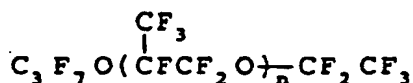
Examples of inert polyfluoropolyether fluids useful in the practice of this invention include those designated by the trade names "Krytox" 1506, "Krytox" 1514, "Krytox" 1645, commercially available from E.I. DuPont de Nemours and Company, "Demnum" fluids, commercially available from Daikin, and "Fomblin" Y and "Fomblin" Z fluids, commercially available from Montecatini-Edison.

Examples of structures of such polymers are as follows:

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"Krytox" fluids:

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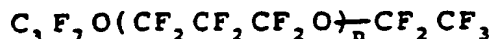
where

$n = 13$  ( for "Krytox" 1506)

$n = 19$  ( for "Krytox" 1514)

$n = 26$  ( for "Krytox" 1645)

5 "Demnum" S-65 fluid:



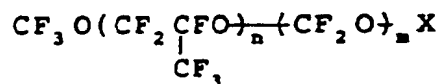
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where

$n = 25$

"Fomblin" Y fluids: Y - VAC 14/6

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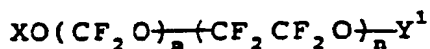
where

$n = 16$

$m = 1$

X represents  $CF_3$ ,  $C_2F_5$ ,  $C_3F_7$ , or  $C_4F_9$

25 "Fomblin" Z fluid:



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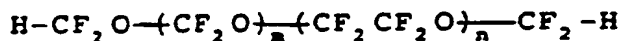
where

$n = 10$  to 100

35  $m = 10$  to 100

X, Y<sup>1</sup> independently represent  $CF_3$ ,  $C_2F_5$ ,  $CF_2Cl$ , or  $CF_2CF_2Cl$

Hydrogen-terminated perfluoropolyether



40

where

$n = 10$

45  $m = 12$

As used herein, the values of m and n represent averages for a distribution of structures. The symbol " $\approx$ " means approximately equals.

Many other inert fluids derived from polyfluoropolyether polymers are useful in this invention.

50 Examples of catalysts and initiators that can be used to crosslink the components of the composition of this invention include dibutyltin diacetate, benzildimethylketal, perfluoroalkylcarboxylic acids, sulfonic acids, and 2-hydroxyl-2-methyl-1-phenylpropane-1-one ("Darocur" 1173, available from EM Industries, Inc.).

Solvents that can be used for applying the composition of this invention include mixtures of the "Freon" series, e.g., 1,1,2-trichlorotrifluoroethane, the "FC" series of perfluorinated hydrocarbons, e.g., perfluorooctane, hexafluoroxylene, and trifluorotoluene.

55 The composition of this invention can be applied to a substrate to form a low energy surface liner by the following process:

(a) providing a solution comprising the functional polyfluoropolyether, the inert polyfluoropolyether, a catalyst for the crosslinking reaction, and a mixture of fluorinated solvents,

(b) coating the solution onto a substrate,

(c) curing the coated composition either thermally or by irradiation, depending on the nature of the curing agent, for a suitable period of time, typically ranging from a fraction of a second to five minutes or more.

Substrate shapes that are suitable for the composition of the present invention include sheets, fibers, and materials of other shapes. Preferred substrate materials include flexible sheet materials that are used as backings for pressure-sensitive adhesive products, such as, for example, polyester, polyimide, polyamide, polyolefin, and polycarbonate films. Other substrate materials that are suitable for the composition of this invention include glass, ceramic, metal, and rubber.

The coating techniques that are useful for applying the composition of this invention include brushing, wire-wound rod or knife coating, spraying, curtain coating, and gravure coating.

In some cases, it may be desirable to first apply to the substrate a primer or an adhesion-promoting coating or to treat the substrate. Such treatments are described in U.S. Patent Nos. 4,567,073 and 4,614,667.

A substrate bearing a coating of the cured composition of the invention on one or both major surfaces thereof can then be coated with any adhesives known in the art, such as, for example, acrylic adhesives, rubber-based adhesives, and silicone-based adhesives. The adhesive-coated substrate can then be wound up into a roll, if desired. Flexible, pressure-sensitive adhesive-coated sheet materials are well known in the art. See, for example, U.S. Patent Re. 24,906 (acrylate), U.S. Patent Nos. 2,857,356; 2,814,601; and 2,736,721 (siloxane), and U.S. Patent No. 3,925,283 (urethane).

The releasability of the coatings of this invention with respect to adhesives can be measured by various methods known in the art. The method selected depends upon whether the final product is in sheet or roll form, such as a tape. Various methods for testing pressure-sensitive tapes are reported by the Pressure-Sensitive Tape Council (PSTC) in "Test Methods for Pressure-Sensitive Tapes".

The release values of the cured polyfluoropolyether-coated substrates prepared in the following examples were determined as follows:

#### Dry Laminate Adhesives

A strip of tape bearing a layer of polysiloxane adhesive was pressed against the surface of a polyfluoropolyether coating under the weight of a 2.3 kg rubber roller to produce a laminate consisting of pressure-sensitive adhesive tape and a polyfluoropolyether-coated substrate. The laminate is then subjected to heat aging. The release value is the force required to separate the layer of adhesive from the release-coated substrate at a peel angle of 180° and a peel rate of 230 cm/min.

#### Adhesives Cast From A Solvent

The adhesive was applied to a polyfluoropolyether-coated substrate by means of a knife coater or other suitable coating device, dried, and cured if required. The exposed surface of the layer of adhesive was then laminated to a polyester film having a thickness of 50 micrometers. Strips having a width of 2.5 cm were cut from this laminate, and the release value was measured as described above.

The readhesion value of the pressure-sensitive tape was determined as follows:

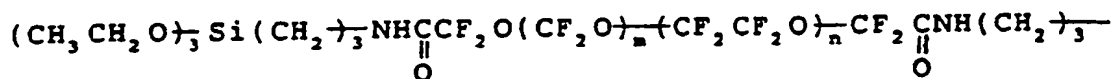
After being removed from the polyfluoropolyether-coated substrate, the pressure-sensitive adhesive was applied to the surface of a clean glass plate by means of a 2.3 kg rubber roller. The readhesion value is a measure of the force required to pull the tape from the glass surface at an angle of 180° at a rate of 230 cm/min.

Advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In the following examples, all values of m and n are average values.

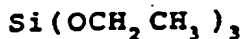
#### EXAMPLE 1

This example demonstrates the effect of inert fluid on the release and readhesion performance of coatings prepared from "Krytox" 1506 polyfluoropolyether fluid or "Krytox" 1514 polyfluoropolyether fluid and a polyfluoropolyether bis(triethoxysilane)(hereinafter Compound I).

( I )



5



10 m = 12

n = 10

Five coating solutions comprising 6% by weight of a mixture of polyfluoropolyether bis(triethoxysilane) (Compound I) and perfluoropolyether fluid in a solvent comprising 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorooctane ("FC-75") were prepared.

15 In the five coating solutions, the ratio by weight of polyfluoropolyether bis(triethoxysilane) to polyfluoropolyether fluid was 95:5, 90:10, 85:15, 80:20, and 70:30. The polyfluoropolyether fluids used were "Krytox" 1506 and "Krytox" 1514 fluids.

A cure catalyst, dibutyltin diacetate (2% by weight, based on total polyfluoropolyether charge), was added to each solution. Release liners were made by coating the aforementioned solutions onto polyethylene terephthalate films (50 micrometers thick) by means of a #4 Mayer bar, thereby producing coatings having a nominal coating thickness of 0.5 micrometers. The liners were cured for about 16 hours at about 25 °C. The cured liners were laminated to 2.5 cm wide strips of adhesive tape having an aggressively tacky methylsilicone pressure-sensitive adhesive ("MacDermid" MACu Tape P-3) by pressing the adhesive into contact with the liner by means of a 2.3 kg rubber roller. The initial values of "Release Peel Force", "Readhesion Peel Force" and "Control Peel Force" were measured by means of a peel tester (3M Model 25 90, available from Instrumentors, Inc.). The 180 ° peel force was measured at a peel rate of 230 cm/min. After being peeled off the liner, the pressure-sensitive adhesive was immediately readhered to a clean glass plate by means of a 2.3 kg hard rubber roller (two passes), and the 180 ° peelback force (the "Readhesion Peel Force") was again measured at a peel rate of 230 cm/min.

30 Another piece of the test tape was adhered to a clean glass plate and tested in the same way as in the previous test to provide the "Control Peel Force". The reduction in "Readhesion Peel Force" versus "Control Peel Force" was presumed to result from transfer of liner material to the pressure-sensitive adhesive. Some of the laminates were aged for 72 hours at 70 °C prior to testing. The test results are set forth in Table I.

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TABLE I

	"Krytox" designation	Ratio of Compound I to fluid	Release force (N/dm)	Readhesion <sup>a</sup> (N/dm)
5	.....	100:0	20.4	30.9
10	1506	95:5	15.5	32.1
	1506	90:10	10.3	31.9
	1506	85:15	1.2	42.0
15	1506	80:20	1.1	42.2
	1506	70:30	0.4	35.4
	1514	95:5	1.2	41.1
	1514	90:10	0.8	43.0
20	1514	85:15	0.4	40.6
	1514	80:20	0.3	37.0
	1514	70:30	0.2	32.7

25 <sup>a</sup> Control readhesion for fresh adhesive was approximately  
 39 N/dm. As used herein, "control readhesion" means  
 30 the adhesion of an adhesive that has never been in  
 contact with a release liner.

EXAMPLE 2

35 This example demonstrates preparation of release coatings for solvent-cast silicone adhesives. Release  
 liners were applied to PET film (50 micrometers) by means of coating with a #4 R.D.S. wire-wound rod a  
 solution containing 6% by weight of a mixture of 83% by weight polyfluoropolyether bis(triethoxysilane)  
 (Compound I) and 17% by weight "Krytox" 1506 fluid in a solvent containing 40% by volume 1,1,2-  
 40 trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorooctane ("FC-75"). The solution also  
 contained 4% by weight dibutyltin diacetate (based on total polyfluoropolyether charge). The coatings were  
 allowed to cure overnight in air at room temperature. Wet-cast silicone adhesives DC-355 and GE-6574  
 were applied to the release coatings under the conditions specified in Table II. After the adhesive had dried  
 and cured, it was laminated to PET film (50 micrometers). Pieces of the laminates of 2.5 cm width were cut  
 45 for release and readhesion measurements. These measurements were made by means of the procedures  
 described in Example 1. The results are set forth in Table II.

50

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TABLE II

Adhesive	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
	Initial	Aged	Initial	Aged
DC-355	0.2 <sup>b</sup>	0.3 <sup>b</sup>	63.2 <sup>b</sup>	64.2 <sup>b</sup>
	0.5 <sup>d</sup>	11.9 <sup>d</sup>	66.9 <sup>d</sup>	61.5 <sup>d</sup>
GE-6574	0.3 <sup>c</sup>	0.2 <sup>c</sup>	99.6 <sup>c</sup>	100.1 <sup>c</sup>
	25.6 <sup>e</sup>	.....	82.7 <sup>e</sup>	.....

<sup>a</sup> Control readhesion for fresh adhesives: DC-355, approximately 82 N/dm; GE-6574, approximately 100 N/dm.

<sup>b</sup> The adhesive was coated from 18% by weight solution in 1,1,2-trichlorotrifluoroethane ("Freon" 113), at a wet film thickness of 250 micrometers. The coating was dried 24 hours at room temperature, no catalyst was used. Initial release measurements were made after heating the laminates for 24 hours at 70°C; aged release measurements were made after 7 days at 70°C.

<sup>c</sup> The adhesive was coated from 33% by weight solution of toluene/xylene with 2% by weight (based on silicone) "Cadox TS-50" initiator, at a wet film thickness 300 micrometers. The coating was dried at 70°C for 10 minutes, then cured for 5 minutes at 150°C. Initial release measurements were made shortly after laminating; aged release measurements were made after heating the laminates for 3 days at 70°C.

<sup>d</sup> These values were obtained using release coatings prepared from coating solutions identical to those described in note b, except with 6% by weight compound I (no "Krytox" 1506 fluid present).

<sup>e</sup> These values were obtained using release coatings prepared from coating solutions identical to those described in note c, except with 6% by weight compound I (no "Krytox" 1506 fluid present).

EXAMPLE 3

5 This example demonstrates the preparation of release coatings having a high content of inert perfluoropolyether fluid.

Six coating solutions consisting of 1.1% by weight mixtures of polyfluoropolyether bis(triethoxysilane) (Compound I) and "Krytox" 1514 fluid in a solvent containing 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorotributylamine ("FC-43") were prepared. In the six coating  
 10 solutions, the ratio by weight of polyfluoroether bis(triethoxysilane) to "Krytox" fluid was 50:50, 25:75, 15:85, 10:90, 5:95, and 0:100. The solutions also contained 4% by weight (based on total polyfluoropolyether charge) dibutyltin diacetate as cure catalyst. These solutions were coated onto PET film (50 micrometers) by means of a #4 R.D.S. wire-wound rod. The coated films were heated at 110°C for one minute and  
 15 allowed to stand at room temperature in air for several hours. The coatings were tested with MacDermid P-3 and DC-355 silicone adhesives by means of the procedures described in Examples 1 and 2, and initial release, release after aging, and readhesion values were measured. The results are set forth in Table III.

TABLE III

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	Percent (wt) "Krytox" 1514 fluid		Adhesive		Release (N/dm)		Readhesion (N/dm)*	
					Initial	Aged	Initial	Aged
25	50		MacDermid		0.3	0.7	33.7	35.3
	50		DC-355		0.2	0.3	73.8	72.4
	75		MacDermid		0.3	0.3	33.8	33.5
30	85		MacDermid		0.2	0.2	32.5	33.1
	85		DC-355		0.4	0.3	74.7	75.4
	90		MacDermid		0.3	1.0	32.0	30.4
	90		DC-355		10.4	...	67.0	...
35	95		MacDermid		0.8	10.3	31.1	21.4
	95		DC-355		15.9	....	68.9	....
	100		MacDermid		31.2	35.7	20.9	22.0
40	100		DC-355		78.4	82.2	25.5	38.3

\* Control readhesion for fresh adhesives: "MacDermid"  
 P-3, approximately 35 N/dm; DC-355, approximately 82  
 45 N/dm.

EXAMPLE 4

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This example demonstrates the effect of concentration of inert perfluoropolyether fluid on performance of release coatings with a solvent-cast peroxide cured adhesive.

Three coating solutions comprising 1.1% by weight mixtures of polyfluoropolyether bis(triethoxysilane) (Compound I) and "Krytox" 1514 fluid, were prepared. In the three coating solutions, the ratio by weight of  
 55 polyfluoropolyether bis(triethoxysilane) to polyfluoropolyether fluid was 83.3:16.7, 75:25, and 67:33. The solution also contained 4% by weight (based on total polyfluoropolyether charge) dibutyltin diacetate as the cure catalyst. These solutions were coated onto PET film (50 micrometers) by means of a #4 R.D.S. wire-wound rod. The coatings were cured at 110°C for one minute and then allowed to stand overnight in air at

room temperature.

Silicone adhesive (DC-7406)(33% by weight solids in toluene) with 2% by weight (based on silicone solids) initiator ("Cadox TS-50") was applied to the release coatings by means of a knife coater (300 micrometers orifice). The adhesive was dried at 70 °C for 10 minutes, cured at 150 °C for five minutes, and laminated to PET film (50 micrometers). Strips of 2.5 cm width were cut for peel test measurements. Initial release, release upon aging (70 °C for 72 hours) and readhesion were evaluated by the procedures described in Example 1. The results are set forth in Table IV.

**TABLE IV**

Weight Ratio of Compound I to "Krytox" 1514 fluid	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
	Initial	Aged	Initial	Aged
83.3:16.7	0.7	27.8	65.0	57.0
75:25	1.2	19.1	73.5	64.4
67:33	0.9	1.1	79.7	82.3

<sup>a</sup> Control readhesion for fresh adhesive, approximately  
77 N/dm

**EXAMPLE 5**

Release coatings were prepared according to the procedures used in Example 4 from 1.1% by weight solutions of mixtures of polyfluoropolyether bis(triethoxysilane) (Compound I) and various polyfluoropolyether inert fluids. Solvent, catalyst, coating conditions, and curing conditions used were identical to those used in Example 4. The coatings were tested according to the procedures described in Examples 1 and 2. The coatings were laminated with silicone adhesives ("MacDermid" P-3 and DC-355), and initial release, release after aging, and readhesion values were measured. The results are set forth in Table V.

TABLE V

Inert fluid	Weight ratio of Compound I to inert fluid	Adhesive	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
			Initial	Aged	Initial	Aged
"Demnum" S-65	67:33	"MacDermid"	0.6	1.6	32.8	32.6
"Demnum" S-65	67:33	DC-355	0.3	0.3	68.1	69.1
PPE (H) <sub>2</sub> <sup>b</sup>	67:33	"MacDermid"	0.4	0.6	35.4	....
PPE (H) <sub>2</sub> <sup>b</sup>	67:33	DC-355	0.2	0.2	84.6	87.5
"Krytox" 1645	75:25	"MacDermid"	1.5	2.5	40.5	36.7
"Krytox" 1645	75:25	DC-355	1.6	2.4	69.5	66.8

<sup>a</sup> Control readhesion for fresh adhesives: "MacDermid" P-3, approximately 34 to 39 N/dm, some variation between lots. DC-355, 82 to 93 N/dm, some variation between lots.

<sup>b</sup> PPE(H)<sub>2</sub> is an abbreviation for hydrogen-terminated perfluoropolyether.

## 55 COMPARATIVE EXAMPLE A

A release coating was prepared according to the procedure described in Example 5 from a 1.1% by weight solution of a mixture of polyfluoropolyether bis(triethoxysilane) (Compound I) and "Braycote" 815Z



inert polyfluoropolyether fluid. The weight ratio of Compound I to the inert fluid was 67:33. Solvent, catalyst, coating conditions, and curing conditions were identical to those of Example 5. The coating was tested with silicone adhesives ("MacDermid" P-3 and DC-355) by means of procedures described in Examples 1 and 2, and initial readhesion and readhesion after aging were measured. The results are set forth in Table VI.

TABLE VI

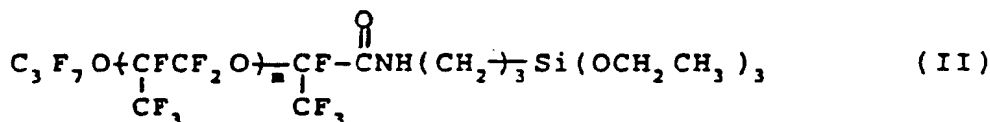
Adhesive	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
	Initial	Aged	Initial	Aged
"MacDermid"	5.1	15.1	31.8	24.2
DC-355	2.7	4.9	63.6	65.5

<sup>a</sup> Control readhesion for fresh adhesives: "MacDermid" P-3, approximately 35 N/dm; DC-355, approximately 82 N/dm

## EXAMPLE 7

This example involves preparation of a release coating using a mixture of monofunctional and difunctional reactive materials.

A coating solution (hereinafter Solution A) consisting of 1.1% by weight of a mixture of polyfluoropolyether bis(triethoxysilane) (Compound I), polyfluoropolyether triethoxysilane (Compound II) (n = 10), and "Krytox" 1514 fluid, was prepared.



m = 10

The weight ratio of Compound I to Compound II to the inert fluid was 1:1:1. Solution A also contained 4% by weight (based on total polyfluoropolyether charge) dibutyltin diacetate as cure catalyst. The solvent consisted of 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorotributylamine ("FC-43").

A second coating solution (hereinafter Solution B) was prepared in a manner identical to that used to prepare Solution A. Solution B consisted of a 1.1% by weight solution of a mixture of Compound I and Compound II in a solvent consisting of 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorotributylamine ("FC-43"). The ratio by weight of Compound I to Compound II was 1:1. No "Krytox" 1514 fluid was added to Solution B. These solutions were coated onto PET film (50 micrometers) by means of a #4 R.D.S. wire-wound rod, heated at 110°C for one minute, then allowed to age in air at room temperature for one week. The coatings were laminated and tested with adhesive tape ("MacDermid" P-3) as described in Example 1. The results from peel measurements are set forth in Table VII.

TABLE VII

Solution	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
	Initial	Aged	Initial	Aged
A	3.4	6.9	33.5	31.5
B	25.2	27.8	27.4	26.2

<sup>a</sup> Control readhesion for fresh adhesive, approximately 35 N/dm

EXAMPLE 8

Coating solutions containing 1.0% by weight of mixtures of polyfluoropolyether bis(triethoxysilane) (Compound I) and "Krytox" 1514 fluid were prepared. The solvent consisted of 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorotributylamine ("FC-43"). The solutions also contained 4% by weight (based on total polyfluoropolyether charge) dibutyltin diacetate. These solutions were coated on polyimide film ("Kapton") (25 micrometers) by means of a #4 R.D.S. wire-wound rod, and cured at 110°C for 10 minutes. After the coatings had cooled, they were laminated to strips of silicone adhesive tape (3M #92, Minnesota Mining and Manufacturing Company) by means of a 2.3 kg rubber roller. The laminates were aged at 130°C for 17 hours before they were tested for release and readhesion values according to the procedures described in Example 1. The results are set forth in Table VIII.

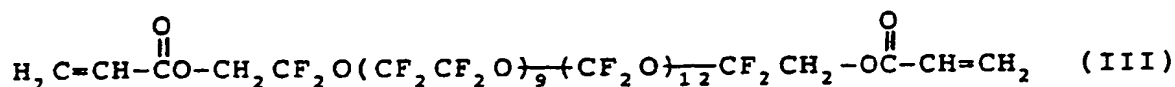
TABLE VIII

Weight ratio of Compound I to "Krytox" 1514 fluid	Release (N/dm)	Readhesion (N/dm) <sup>a</sup>
100:0	20.5	26.5
90:10	15.7	25.4
80:20	13.6	24.5
70:30	5.5	25.2

<sup>a</sup> Control readhesion for fresh adhesive, approximately 26 N/dm

EXAMPLE 9

This example describes the preparation of ultraviolet radiation-cured release coating prepared from "Krytox" 1514 fluid and polyfluoropolyether diacrylate (Compound III).



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Coating solutions consisting of 1.1% by weight of 100% polyfluoropolyether diacrylate (Compound III) and a mixture of 67% by weight Compound III and 33% by weight "Krytox" 1514 fluid in a solvent consisting of 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume per-  
 10 fluorotributylamine ("FC-43") were prepared.

These solutions were coated onto PET film (50 micrometers) by means of a #4 wire-wound rod. Curing was effected by two passes of each coated substrate through a PPG Model 1202 ultraviolet processor at a line speed of 20 m/min, in a nitrogen atmosphere, and at a high lamp power. The coatings were laminated to silicone adhesive tape ("MacDermid" P-3) and the laminates were tested for release and readhesion  
 15 values according to the procedures described in Example 1. The results are set forth in Table IX.

**TABLE IX**

20

Weight ratio of Compound I to "Krytox" 1514 fluid	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
	Initial	Aged	Initial	Aged
67:33	0.3	0.8	32.6	28.7
100:0	2.7	20.7	36.5	24.9

25

<sup>a</sup> Control readhesion for fresh adhesive, approximately  
 30 35 N/dm

**EXAMPLE 10**

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This example describes the preparation of ultraviolet radiation-cured release coatings with added photoinitiator.

Three coating solutions consisting of 6.0% by weight of mixtures of polyfluoropolyether diacrylate  
 40 (Compound III) and "Krytox" 1514 fluid, along with 2% by weight (based on total polyfluoropolyether charge) "Darocur" 1173 photoinitiator, in 1,1,2-trichlorotrifluoroethane ("Freon" 113) were prepared. The ratio by weight of Compound III to "Krytox" 1514 fluid in the three mixtures was 100:0, 85:15, and 70:30. The coatings were applied, cured, and tested in accordance with the procedures described in Example 9. The results are set forth in Table X.

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TABLE X

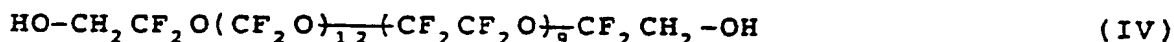
Weight ratio of Compound I to "Krytox" 1514 fluid	Release (N/dm)		Readhesion (N/dm)*	
	Initial	Aged	Initial	Aged
85:15	0.3	1.4	34.1	33.2
70:30	0.2	0.5	33.0	29.5
100:0	0.2	17.0	37.8	26.0

\* Control readhesion for fresh adhesive, approximately 35 N/dm

#### EXAMPLE 11

This example describes preparation of release coatings based on urethane-cure chemistry.

A coating solution (hereinafter Solution C) was prepared by mixing, in a vial, polyfluoropolyether diol (Compound IV) (0.85 g), toluenediisocyanate (0.12 g), "Krytox" 1514 fluid (0.32 g), and 1,1,2-trichlorotrifluoroethane ("Freon" 113) (20.2 g).



After the mixture was shaken to form a solution, dibutyltin diacetate (0.022 g) was added thereto. A coating solution (hereinafter Solution D) was prepared by mixing, in a vial, polyfluoropolyether diol (Compound IV) (1.13 g), toluenediisocyanate (0.16 g), and 1,1,2-trichlorotrifluoroethane ("Freon" 113) (20.2 g). After the mixture was shaken to form Solution D, dibutyltin diacetate (0.022 g) was added thereto. Solution C and Solution D were coated on PET film (50 micrometers) by means of a #4 R.D.S. wire-wound rod, and the coatings were cured at 110°C for five minutes. After the coatings aged overnight in air at room temperature, they were tested with silicone adhesive (DC-355) according to procedures described in Example 2. Release and readhesion results are set forth in Table XI.

TABLE XI

Coating	Release (N/dm)		Readhesion (N/dm)*	
	Initial	Aged	Initial	Aged
Solution C	1.4	2.0	60.2	58.1
Solution D	32.5	49.4	58.3	53.3

\* Control readhesion for fresh adhesive, approximately 82 N/dm

#### EXAMPLE 12

This example describes the use of a polyurethane substrate.

A coating solution (hereinafter Solution E) was prepared by mixing, in a vial, polyfluoropolyether diol (Compound IV) (0.88 g), toluenediisocyanate (0.15 g), "Krytox" 1514 fluid (0.26 g), and 1,1,2-trichlorotrifluoroethane ("Freon" 113) (20.15 g). After the mixture was shaken to form a solution, dibutyltin diacetate (0.052 g) was added. A coating solution (hereinafter Solution F) was prepared in the same way from polyfluoropolyether diol (Compound IV) (1.10 g), toluenediisocyanate (0.19 g), trichlorotrifluoroethane ("Freon" 113) (20.15 g), and dibutyltin diacetate (0.052 g). These solutions were coated on "Gravel Guard" polyurethane film by means of a #4 R.D.S. wire-wound rod. The coatings were cured at 110°C for five minutes, then allowed to age overnight in air at room temperature. They were laminated to strips of silicone adhesive tape ("MacDermid" P-3), and the laminates were tested to determine initial release, release after aging, and readhesion according to the procedures described in Example 1. The results are set forth in Table XII.

TABLE XII

Coating	Release (N/dm)		Readhesion (N/dm) <sup>a</sup>	
	Initial	Aged	Initial	Aged
Solution E	0.2	6.6	33.5	23.5
Solution F	21.9	38.1	27.7	22.7

<sup>a</sup> Control readhesion for fresh adhesive, approximately 35 N/dm

## EXAMPLE 13

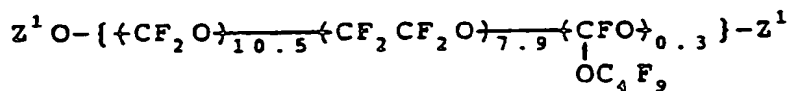
This example describes the overcoating of inert fluid on a coating of the curable component.

Polyfluoropolyether bis(triethoxysilane) (Compound I) was coated onto PET film (50 micrometers) and cured in the identical manner as described in Example 1. After the coating was cured overnight at room temperature, it was overcoated with a solution of 1% by weight "Krytox" 1506 fluid in perfluorooctane ("FC-75") by means of a #4 R.D.S. wire-wound rod. After the solvent had evaporated, the composite coating was laminated to strips of silicone adhesive ("MacDermid" P-3) and the laminates were tested to determine initial release, release after aging, and readhesion by means of the procedures of Example 1. The results were as follows. Release: Initial, 0.1 N/dm; aged, 0.2 N/dm. Readhesion: Initial, 38.1 N/dm; aged, 39.4 N/dm. The control readhesion of a fresh adhesive was approximately 39 N/dm.

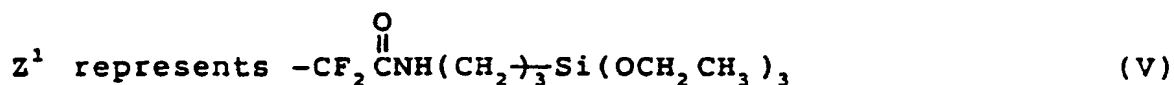
## EXAMPLE 14

This example describes the use of crosslinkable perfluoroether polymer with pendant perfluoroether groups attached to the backbone.

A coating solution consisting of 0.97% by weight of a 1.7:1.0 mixture of polyfluoropolyether bis(triethoxysilane) (Compound V) and "Krytox" 1514 fluid along with 4% by weight (based on the total polyfluoropolyether) dibutyltin diacetate as a cure catalyst in a solvent consisting of 40% by volume 1,1,2-trichlorotrifluoroethane ("Freon" 113) and 60% by volume perfluorotributylamine ("FC-43") was prepared.



where



5

This solution was coated on PET film (50 micrometers) by means of a #4 R.D.S. wire-wound rod, and the coating was cured at 100°C for five minutes and then allowed to stand overnight in air at room temperature. The coating was tested with silicone adhesive (DC-355) according to the procedure described in Example 2. The results were as follows. Release: Initial 0.2 N/dm; aged 0.2N/dm. Readhesion: Initial 78.7 N/dm; aged 78.3 N/dm. The control readhesion of fresh adhesive was approximately 82 N/dm.

In the preceding examples, the trademarks and tradenames set forth therein were obtained from the source listed in Table XIII.

15

TABLE XIII

<u>Trademark or trade name</u>	<u>Source</u>
MACu P-3 Tape	MacDermid Co. Inc.
"Freon" 113	E.I. DuPont de Nemours and Company
"Krytox" fluids	E.I. DuPont de Nemours and Company
"Kapton" film	E.I. DuPont de Nemours and Company
"FC" series solvents	Minnesota Mining and Manufacturing Company
Gravel Guard PU film	Minnesota Mining and Manufacturing Company
DC-355	Dow-Corning Inc.
DC-7406	Dow-Corning Inc.
GE-6574	General Electric Inc.
"Cadox TS-50"	Noury Chemical Co.
"Demnum" fluids (Tokyo, Japan)	Daikin Industries
"Braycote" 815Z	Bray Oil Co.
PPG Model 1202 UV	Pittsburgh Plate Glass Co.
"Darocur" 1173	EM Industries Inc.

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Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

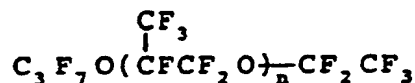
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**Claims**

1. A composition suitable for preparing a release coating comprising a polyfluoropolyether containing at

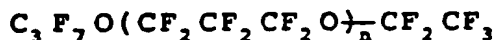
least one reactive group and an inert polyfluoropolyether oil.

2. The composition of Claim 1, wherein the inert polyfluoropolyether has a viscosity of from about 20 to about 500 centipoise at 25° C.
- 5 3. The composition of Claim 1, wherein the inert polyfluoropolyether has a viscosity of from about 90 to about 200 centipoise at 25° C.
- 10 4. The composition of Claim 1, wherein the polyfluoropolyether containing at least one reactive group is capable of crosslinking or polymerizing or both.
5. The composition of Claim 4, wherein the reactive group of the polyfluoropolyether is selected from the group consisting of acrylate, hydrosilane, silanol, silalkoxy, epoxy, and isocyanate.
- 15 6. The composition of Claim 1, wherein the inert polyfluoropolyether oil is:



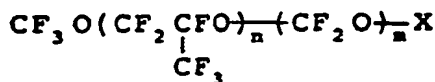
where  
n = 13, 19, or 26.

- 25 7. The composition of Claim 1, wherein the inert polyfluoropolyether oil is:



where  
n = 25.

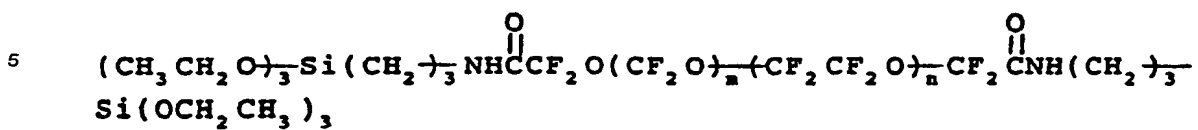
- 35 8. The composition of Claim 1, wherein the inert polyfluoropolyether oil is:



where  
n = 16  
m = 1  
X represents CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>, or C<sub>4</sub>F<sub>9</sub>.

9. A solution comprising the composition of Claim 1 and a solvent selected from the group consisting of evaporable fluorocarbons, chlorofluorocarbons, and mixtures thereof, the viscosity of the solution being sufficiently low to permit the deposition of a thin, continuous coating upon a substrate.
10. A substrate bearing a coating formed from the composition of Claim 9, wherein said coating has been crosslinked by thermal or actinic energy.
- 55 11. Tape comprising a backing bearing on one major surface thereof a layer of pressure-sensitive adhesive and on the other major surface thereof a release coating prepared from the composition of Claim 1.
12. The tape of Claim 11, wherein said pressure-sensitive adhesive comprises a silicone polymer.

13. The composition of Claim 1, wherein the polyfluoropolyether containing at least one reactive group

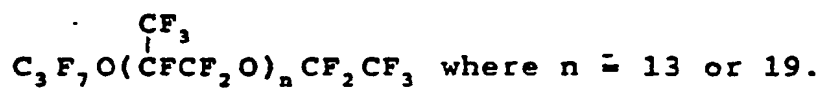


is where

$$m = 12$$

$$n = 10$$

and the inert polyfluoropolyether oil is





(19)



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**St. Paul, Minnesota 55133-3427(US)**(74) Representative: **Baillie, Iain Cameron et al**  
**c/o Ladas & Parry Alzheimer Eck 2**  
**W-8000 München 2(DE)**(54) **Fluorocarbon-based coating compositions and articles derived therefrom.**

(57) This invention relates to release liners, and more particularly, to release liners suitable for use with highly aggressive pressure-sensitive adhesives. Certain pressure-sensitive adhesives, particularly those derived from silicone resins, are so aggressive that tapes employing them exhibit undesirably high peel forces upon removal from known low-adhesion coatings, especially after prolonged storage or when used in a high-temperature environment. The adhesive of such tapes may carry away, and consequently, be contaminated by appreciable amounts of the low-adhesion material. If this occurs, the tapes will exhibit poor readhesion when applied to "end-use" receptor surfaces. This invention provides curable, crosslinkable compositions and coatings prepared therefrom that can be used to form low-surface energy liners that can be used with aggressive pressure-sensitive adhesives, such as adhesives formed from silicone resins. The release characteristics of these coatings do not diminish upon aging and do not adversely affect the readhesion properties of adhesives that have come in contact with the coatings. The invention further provides substrates bearing a layer of the composition of the invention. These coated substrates are particularly suitable for release liners, especially differential re-

lease liners and low-adhesion backsizes for pressure-sensitive adhesive tapes and sheet materials, especially for pressure-sensitive adhesives derived from silicone resins. Because the coatings of this invention can have more than 50% by weight inert oils without significantly reducing the readhesion of adhesives removed from them, they provide an economic advantage over those coatings prepared by using only the more expensive reactive group-containing polyfluoropolyethers.

**EP 0 433 070 A3**



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## EUROPEAN SEARCH REPORT

Application Number

**EP 90 31 3595**

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	CHEMICAL ABSTRACTS, vol. 113, no. 23, 3 December 1990, Columbus, Ohio, US; abstract no. 213979Q, T.NAKAMURA ET AL.: 'Fluoropolymer release coating com- positions' page 97 ;column 1 ; - - -	1-13	C 09 D 171/00
A	EP-A-0 098 698 (MINNESOTA MINING AND MANUFAC- TURING COMP.) * page 5, line 26 - page 10, line 5; claims ** - - -	1	
A	US-A-4 830 910 (J.M.LARSON) * column 9, line 4 - column 15, line 20 ** - - -	1	
D,A	US-A-4 567 073 (J.M.LARSON) * column 4, line 6 - column 7, line 15; claims ** - - - - -	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 D C 09 J
Place of search		Date of completion of search	Examiner
The Hague		06 November 91	WEIS R.E.
CATEGORY OF CITED DOCUMENTS			
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T: theory or principle underlying the invention			